

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:

Confirmation No.: 9293

Achim WEBER, *et al.*

Serial No.: 10/500,425

Group Art Unit: 1641

Filed: September 7, 2004

Examiner: Melanie J. Yu

For: IMPROVED STRUCTURED-FUNCTIONAL BINDING MATRICES FOR
BIOMOLECULES

VIA EFS-WEB

Commissioner for Patents

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Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. §1.132

Sir:

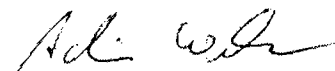
1. I, Achim Weber, am a German citizen, residing at Bachstrasse 40, 73776 Altbach, Germany. I am a co-inventor of the above-identified U.S. patent application. As detailed below, I am employed by Fraunhofer Institute for Interfacial Engineering & Biotechnology, the owner by Assignment of the above-identified application. I have read and am familiar with the U.S. Patent Office Action dated January 6, 2009 concerning the subject application. I understand that the Examiner has rejected certain claims of the application as being allegedly obvious to one having ordinary skill in this art over the combined disclosure of Published U.S. Patent Application No. 2002/0127574 of Mirkin et al. and U.S. Patent No. 7,045,087 of Kotov. I am making this declaration to support the patentability of the claims of the above-identified application.
2. In December 1995 I received a Dipl.-Chem. degree from Stuttgart University located in Stuttgart, Germany. Thereafter, in June 1999 after further study I was granted a Doctorate degree (Dr. rer. nat.), also by Stuttgart University.
3. With regard to my relevant employment experience, I was employed from September 1995 to August 1999 as a lecturer while I was a Ph.D. student at Stuttgart University. Thereafter, from September 1999 to December 1999 I engaged in postdoctoral work in the laboratory of Prof. Bayer at the Research Center of Nucleic Acids and Peptides at Tübingen University in Tübingen, Germany. From January 2000 to September 2002 I undertook additional postdoctoral studies at the University of Stuttgart in the Institute of

- Interfacial Engineering IGVT, where I was employed as a Project Manager in the area of Biomimetic Surfaces. From October 2002 until November 2006 I worked for the Assignee, Fraunhofer Institute for Interfacial Engineering & Biotechnology IGB, as a Project Manager. Since December 2006 I have been employed at the above-cited Fraunhofer Institute as a Group Manager in the area of Biomimetic Functional Films.
4. The Examiner alleges that Kotov U.S. Patent No. 7,045,087 teaches a functional element wherein the bonding agent is a plasma layer with charged chemically reactive groups, as is presently recited in, e.g., claim 1 of the above-identified application. In response, I submit that bonding layers produced according to the method outlined in the '087 Kotov patent are produced with the use of "layer by layer" (LBL) technology that does not involve or include any plasma polymerization. As discussed further below, bonding layers produced with LBL technology (i.e., according to the Kotov reference) demonstrate significant differences in regard to both their structure(s) and their properties in comparison to plasma-formed layers with chemically charged reactive groups as recited in, e.g., claim 1 of this application. The above distinction(s) holds true, moreover, just as much for a single LBL layer as it does for a cross-linked stack or 'laminate' of such LBL layers.
 5. As our Counsel have previously pointed out, i.e., in the Response filed October 14, 2008 (see, e.g., p. 15) I, as one having at least an ordinary level of skill in this field, am well aware that plasma-polymerized bonding layers, i.e., in accordance with claim 1, are known to be highly irregular in terms of their structure. Such structure is deemed by those knowledgeable in this field to be an amorphous structure. In contrast, however, layers formed according to the LBL technique disclosed in Kotov have well-ordered crystalline structures. They are, thus, not highly irregular. In fact, the LBL layers are typically very regular and very well organized into stratified thin films in a specific predetermined order. See, e.g., Kotov at Col. 1, lines 53-56. Therefore, their structure can not be characterized as 'amorphous'. As indicated in the paragraph above, it is well known among those working in this field that the substantial differences in the structure of plasma-formed layers versus LBL layers (i.e., as noted above) leads to substantial differences in the properties of these layers.
 6. The characterization in the paragraph above of the structural features of layers prepared by plasma polymerization, i.e. as claimed in the present application, is further supported by the disclosure contained in the attached reference, Gaur et al., "Plasma Polymerization: Theory and Practice", 43rd Annual Technical Conference Proceedings, Society of Vacuum Coaters, pp. 267-271 (2000). In the last paragraph of col. 1 on p. 267, the reference states that hexamethyldisiloxane (HMDSO) films prepared by plasma

polymerization were found to be, "amorphous and pinhole free". The reference then additionally states, in the first column on p. 268, that plasma polymers do not contain regular repeating units and that the chains are branched and randomly terminated with a high degree of cross-linking. Further according to the reference, the chemical reactions that occur under plasma conditions are generally very complex and are non-specific in nature. This, then, completely supports the characterization above of the plasma-formed layers as being highly irregular and with an amorphous structure, i.e., in contrast to the LBL layers which, as also noted above are regular and which have crystalline structures.

7. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 31.03.09

By: 
Dr. Achim Weber

Plasma Polymerization: Theory and Practice

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Key Words: Plasma polymerization
Magnetron

Film thickness
Polymer films

ABSTRACT

Plasma polymerization of hexamethyldisiloxane (HMDSO) monomer has been carried out at 40kHz-magnetron discharge. The presence of magnetron causes electrons to move in spirals instead of straight lines which increases the frequency of collisions and hence fragmentation, resulting in dense polymer film deposits at lower pressures. HMDSO is a choice of industries because of its volatility, cheap availability and relatively non-toxic nature.

Plasma polymerization depends on monomer flow rate, system pressure and discharge power among other variable parameters. In this work, film growth has been studied by thickness measurements with respect to change in flow rate of the monomer and applied power. The deposition rate, at constant power, increases at first and then decreases with further increase in flow rate. Plasma polymerization of HMDSO can be carried out at low temperatures which makes it possible to coat plastics without any thermal damage.

INTRODUCTION

Plasma polymerization is gaining importance for last several years as a tool to modify material surfaces. Organic vapors can be polymerized at low temperatures using plasma enhancement. Plasma polymerization can also be used to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions because such processes involve electron impact dissociation and ionization for chemical reactions.

Organosilicone films prepared by plasma polymerization provide good optical and mechanical properties [1-4]. Most used monomers in this family of compounds include tetramethylsilane, vinyltrimethylsilane, HMDSO and hexamethyldisilazane containing Si, H, C, O or N atoms.

HMDSO is a choice of industries because it is a non-toxic material and no harmful materials are produced during processing. It can be used in production environment without any special safety considerations. Basic research studies on plasma polymerized organosilicones are reviewed by various authors [5-7]. The films were found to be amorphous and pinhole free.

Various applications [8-11] of plasma polymer films include anticorrosive surfaces, humidity sensors, electrical resistors, scratch resistance coatings, optical filters, protective coatings, chemical barrier coatings, etc. Metallized surfaces of synthetic materials can be protected against corrosion with a thin polymer layer deposited by plasma polymerization. The processes can be customized to produce hydrophobic or hydrophilic (antifogging effect) coatings. Scratch resistant coatings have been successfully applied on optical lenses but three-dimensional objects, such as reflectors for the motor car and lighting industries are complicated by the fact that power input may not be uniform over the entire substrate surface during the polymerization process [12].

A magnetron based plasma polymerization process is described here with HMDSO as the active ingredient. Deposition rate, power input, system pressure and chemical analysis results are discussed.

THEORY

Plasma polymerization takes place in a low pressure and low temperature plasma that is produced by a glow discharge through an organic gas or vapor. Plasma polymerization depends on monomer flow rate, system pressure and discharge power among other variable parameters such as the geometry of the system, the reactivity of the starting monomer, the frequency of the excitation signal and the temperature of the substrate. Various plasma polymer deposition methods such as DC, AF-magnetron and RF are discussed by Yasuda et al. [13].

The overall power input in plasma polymerization is used for two things: for creating the plasma and for fragmentation of monomer. Plasma is a direct consequence of the ionization of the gases present in the reactor and fragmentation leading to polymerization is secondary process. As increasing voltage is applied between two parallel plate electrodes, an abrupt increase in current implies the breakdown of the gases in between the electrodes. High-energy electrons collide with hydrocarbon molecules to produce positive ions, C^+ , CH^+ , CH_2^+ etc., excited molecular or atomic fragments, radicals, new compounds etc. Positive ions are accelerated towards cathode and produce secondary electrons in the process.

Excited atoms emit photons and create glow. Since remaining positive ions also flow towards cathode, the most intense glow in the reactor is at cathode.

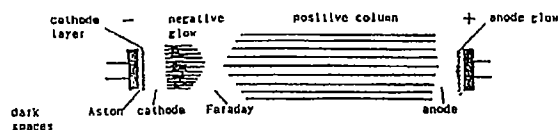


Figure 1. Normal glow discharge, Reprinted from [7], with permission from Elsevier Science.

The positive column (space spread between cathode and anode) containing electrons, ions and radicals, is electrically neutral. This is plasma but most people call glow discharge, the plasma. The major polymer deposition occurs onto the substrate surface that makes contact with the glow. Not all glow discharges yield polymer deposition though. The plasmas of Ar, Ne, O₂, N₂ are non-polymer forming and as such can be used to maintain the glow in the vacuum chamber while the monomer vapor is used efficiently for polymer conversion. A review on glow discharge polymerization was written by Yasuda [14].

Although plasma polymerization occurs predominantly in the glow region, the volume of glow is not always the same as the volume of the reactor. Both volume of glow discharge and the intensity of glow also depend on the mode of discharge, the discharge power and the pressure of the system. Under plasma conditions, the monomer molecules undergo fragmentation and deposit as polymer molecules, and a non-polymer forming by-product like hydrogen gas is evolved. Therefore plasma polymerization of an organic monomer acts as a pump. The plasma polymer does not contain regularly repeating units, the chains are branched and are randomly terminated with a high degree of crosslinking. They adhere well to solid surfaces. Pyrolysis results of plasma-polymerized organosilicones [15] suggest a cationic oligomerization from the electron bombardment of the monomer followed by UV-initiated crosslinking in solid phase to give the final product.

Chemical reactions that occur under plasma conditions are generally very complex and nonspecific in nature. Glow discharge polymerization of organic compounds seems to proceed by the free radical mechanism [11,16] and the extent of ionization is small. The combination and recombination of these radicals form high molecular weight compounds called polymers. The free radicals are trapped in these films which continue to react and change the polymer network over time. Since radicals are formed by fragmentation of monomer, some elements and groups may be absent in resulting polymer. The degree of fragmentation depends on electron density or input power and monomer flow rate. Crosslinking reactions occur on the surface or in the bulk of the newly forming plasma

polymer between oligomers. The film may also change due to reaction with oxygen and water vapor in atmosphere.

Although, the polymer deposition rate is linearly dependent on the current density [17], the minimum wattage necessary for the plasma polymerization of a given monomer differs significantly from another. This is because discharge power needed to initiate glow discharge varies from one monomer to another. The crosslinking in plasma polymer increases with the intensity and energy of bombarding ions. If the inter-electrode distance is too large, then, at a given applied potential, the local electric field in the plasma will be too low to deliver sufficient energy to the electrons. The atoms in a vacuum travel in straight lines. If there is residual gas in the chamber, the atoms will collide with the gas and would go in all directions losing some energy as heat. At higher pressures, the collisions will cause atoms to condense in air before reaching the substrate surface giving rise to powder deposits.

A magnetically enhanced audio frequency discharge is reported [18] to have some advantages for plasma polymerization. Magnetron, as this is called, is a properly shaped, intense magnetic field which traps electrons in an electric field and cause them to move in spirals instead of straight lines [7]. This increases the frequency of collision between electrons and gas molecules, causing more fragmentation, higher deposition rates and dense polymer deposits at lower pressures.

EXPERIMENTAL

All experiments were carried out in a 30-inch diameter round vacuum chamber which was pumped through a rotary vane pump for roughing and a diffusion pump for high vacuum. The chamber pressure was measured by either a Balzer's gauge or a convectron gauge. 7 inch, over the counter, round magnetrons with stainless steel (SST) plates were used as electrodes. HMDSO was heated thermostatically to 130°F and only vapors were drawn through a mass flow controller into the chamber. A 40kHz AC power supply (Advanced Energy PE II) was used to supply power to the chamber. The chamber was pumped down to 2×10^{-4} Torr and was back-filled with monomer vapor before turning the power on. The substrates attached to a fixture were spinned for uniformity of the coating. Experiments were carried out at various flow rates of monomer, various power inputs and in presence /absence of an inert gas Helium.

Thickness of the polymer films (PP-HMDSO) deposited on a glass slide was measured with a Tencor P10 Profilometer. Polymer films were also deposited on aluminium coated polycarbonate slides for corrosion testing with 2% NaOH solution. The results are presented and discussed in following paragraphs.

Chemical analysis of samples were done by X-ray photoelectron spectroscopy (XPS) to determine elemental concentra-

tions and identify their chemical environment. Typical analytical conditions for the double pass cylindrical mirror analyzer of the XPS system were a Pass energy of either 25eV or 50eV and an analytical area of 4mm. The X-ray source was Mg anode (1253.6eV) at 300W. The entire system was calibrated using gold and copper standards.

RESULTS AND DISCUSSION

Deposition rate vs flow of monomer

Deposition rate of PP-HMDSO increases with the flow of monomer at first and then decreases. Yasuda [5] has called the first part of such plot as monomer deficient region and second part as energy deficient region. He has also mentioned that the initial monomer deficient region can be increased by increasing the power input. In Figure 2 we received typical monomer deficient and energy deficient regions for the power input of 2200W.

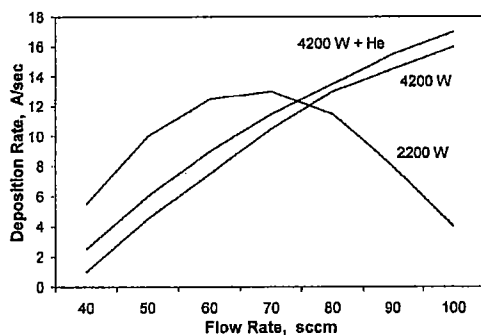


Figure 2. Deposition rate of PP-HMDSO as a function of monomer flow rate in magnetron discharge.

In order to observe the effect of increase in power on deposition rate, experiments were carried out at 4200W. We did receive an increase in linear region but the overall deposition rate was lower. It was found that for same flow rates the processing pressures were higher, may be due to change in pumping efficiency, giving lower mean free path for deposition, hence lower deposition rates. Also, the XPS results show peaks of Fe, Cr, and Ni in the film, probably from the sputtering of SST plates in magnetrons which will influence process pressure and pumping efficiency too. The effect of adding a non-polymer forming inert gas to the system was studied by flowing Helium together with HMDSO vapor. The deposition rate increased slightly showing more efficient use of monomer for polymerization as Helium kept the glow discharge going.

Deposition rate vs power input

Polymer deposition rates plotted against discharge wattage (Figure 3) show that deposition rates level out as input power is increased.

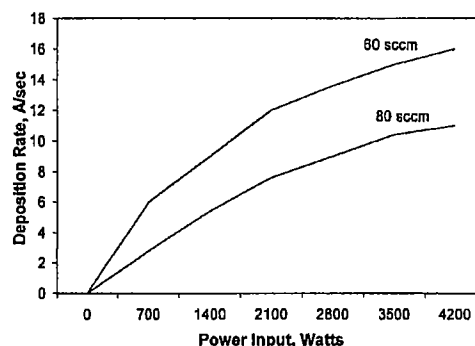


Figure 3. Deposition rate of PP-HMDSO as a function of power input in magnetron discharge.

Various reactions that takes place during plasma polymerization include excitation, ionization, homolytic bond splitting, molecular fragmentation etc. For a low level of energy input, the extent of ionization is low and ion-molecule reactions dominate polymer formation resulting in deposition rate increase with power [19]. Above certain levels of energy, there is greater loss of functional groups from the monomer resulting in competitive polymerization and ablation. Oxygen containing compounds show a tendency to evolve reactive oxygen atoms from their structure. At higher power the free radical reactions become more important in polymer formation. [5,20].

pG/p0 vs power input

Not all glow discharges yield polymer deposition. The plasmas of Ar, Ne, O₂, N₂ are nonpolymer forming. It can be seen that no pressure change is observed when discharge is initiated in presence of e.g. Ar only but if the starting material (monomer) leaves the gas phase (plasma) and deposits as solid polymer, the system pressure will change.

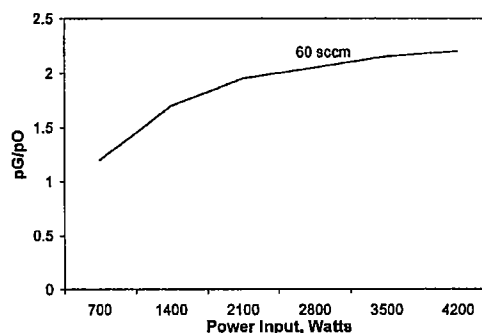


Figure 4. pG/p0 vs Power Input at 60 sccm flow rate of monomer.

In a given flow system, the system pressure (pO) is established at constant temperature as a function of feed-in flow rate and the pumping rate. This situation changes when the monomer is subjected to a glow discharge. Under these conditions the pressure (pG) is a function of monomer flow rate, the pumping rate of the leaving gases and the glow discharge reactions. The polymerization is responsible for pressure drop and ablation and sputtering in this case, contribute to pressure increase. The polymer film growth is the result of two competitive processes, i.e., ablation and deposition [19]. The ablation will apply to both solid phase polymer and to fragmentation of gas phase species. Organosilicone structure is built up of two units: the organic groups like methyl groups are attached to inorganic framework, Si - O - Si. The pressure increase during plasma polymerization (Figure 4) of organosilicone is mainly due to the splitting off of organic groups, whereas the inorganic part of the molecule does not undergo significant fragmentation in the deposition process.

Corrosion testing and visual testing results

Chemical resistance is characterized by exposing the films to NaOH solutions (2%) or similar chemicals. We subjected our films to corrosion testing by putting a drop of 2% NaOH solution on them and timing for penetration by observing dissolution of aluminium layer. We also observed the color of films after processing visually and the results are tabulated in Table 1. It seems that the color in films may be coming from sputtering of SST target.

Table 1. Results of corrosion testing and visual testing.

POWER, Watts	2% NaOH	FILM COLOR
700	30 sec	Clear
1400	30 sec	Clear
2200	30 sec	Clear
3200	45 sec	Yellow
4200	30 sec	Yellow

XPS Analysis

Samples were sputter cleaned at low Ar ion voltages (1kV) and sputter etched using 5kV Ar ions to establish film properties deep into the film. XPS spectra of the polymer film is shown in Figure 5 and the elemental analysis results are listed in Table 2. The PP-HMDSO film contains Si, C, O together with N, Cr, Fe, Ni, and Na. The latter ions might be from sputtering of SST magnetron and air leak in chamber.

Table 2. XPS elemental analysis results.

ELEMENT	PEAK POSITION	% CONCENTRATION	
		As Received	5 min. etched
Si	101.7	8.6	19.8
C	284.6 & 287.0	47.2	15.0
O	531.8	32.7	48.8
N	398.6	8.0	9.4
Cr	577	1.5	4.1
Fe	710.5	1.0	1.7
Ni	852.9	0.4	0.6
Na	107.3	0.7	0.7

The analysis results also suggest that the bulk of the polymer was more oxidized than the surface layer. Silicon is highly reactive with oxygen and will preferentially form SiO compounds [1,21-22]. The atomic ratio of Si:O:C in PP-HMDSO as calculated by XPS elemental analysis is 10:25:8 as opposed to that of the monomer as 10:5:30.

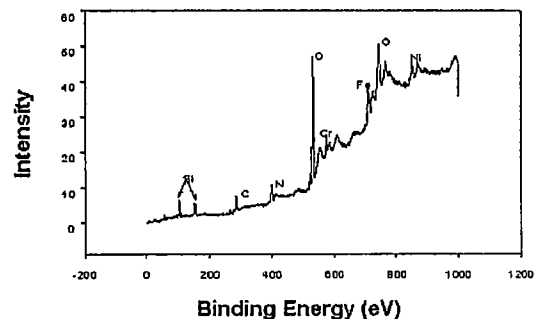


Figure 5. XPS spectra of SST magnetron polymer of HMDSO.

The oxygen peak at 533eV is characteristic of Si-O bonds (SiO₂ gel has a peak at 532.9eV). The carbon peak at 284eV is characteristic of CH₃- group and Si peak at 102.1eV match energies expected for R-Si-O- type silicones. A small peak for carbon at 287eV may be from CO₃²⁻, which means most other metals were present as carbonates. It also explains higher oxygen percentage in analysis. The Si:O:C ratios in polymer film suggest Si-O bonds formed and Si-C bonds broken during processing, releasing hydrocarbons.

CONCLUSION

Magnetron Plasma Polymerization results were presented in this paper with respect to flow rate of monomer, power input, XPS analysis of the film etc. It seems that the film had Si, O, C as main elements but target sputtering was present which added Fe, Cr, Ni and color to the film. Corrosion protection of the film was also not to the desired level. Another process is

since developed in our labs which provides a better quality film. In any event, plasma polymerization can be used to synthesize materials with custom surface chemistries.

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ACKNOWLEDGEMENT

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